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Synthesis and Characterization of Isotactic Polystyrene-
Polybutadiene Block Copolymers

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Synthesis and Characterization of Isotactic Polystyrene/Polybutadiene Block Copolymers

Abstract

Diblock copolymers of isotactic polystyrene and 1,4 polybutadiene were successfully synthesized by two methods: a) coupling of two endfunctionalized homopolymers, and b) sequential synthesis of the two blocks. The polybutadiene blocks were prepared by anionic synthesis yielding ≈ 90% 1,4 (cis-trans) and ≈10% 1,2 addition. The preparation of the isotactic polystyrene block involved a novel anionic polymerization technique using low temperatures and the addition of BuOLi for stereospecific placement. Overall isotactic yields of ≈ 10% by weight were obtained, the remainder being unreacted monomer (50%) and atactic material (40%). The polymers were characterized by GPC, NMR and DSC to determine molecular weights, tacticity and percent crystallinity. The block-like nature of the copolymer was further analyzed through transmission electron microscopy.

INTRODUCTION

Recent efforts in our laboratory have been directed toward the study of diblock copolymers where one or both of the blocks are crystallizable, as in the case of isotactic polypropylene/polybutadiene[1], and isotactic polypropylene/ isotactic polystyrene[2]. These studies are aimed at gaining an understanding of how the extra dimension of crystallinity affects both morphology and properties of the copolymer material. The most recent focus of our research involves the synthesis of a block copolymer, comprised of isotactic polystyrene/polybutadiene blocks; this choice of iPS/PBD was based on the fact that a large amount of work has been carried out in our laboratory and elsewhere on the amorphous analog polymers, atactic polystyrene/polybutadiene.

Various synthesis routes were considered for the block sequences. For the amorphous polybutadiene block, anionic synthesis by means of n-BuLi initiator in a non-polar solvent was the clear choice. The synthesis of isotactic polystyrene

was a more complex problem. This type of stereospecific chemistry commonly involves some type of Ziegler-Natta catalyst in order to achieve the desired tacticity. While this would results in high degrees of conversion and more than 90% desired tacticity, the method does suffer from serious drawbacks when a block copolymer is considered; most of the isotactic chains formed in the Ziegler-Natta polymerization are not active or "living", and cannot therefore be used in the sequential preparation of a diblock copolymer. Endfunctionalization of isotactic polystyrene synthesized by Ziegler-Natta catalysts was considered and rejected as a feasible route in favor of the methods discussed below. We also considered and rejected the possibility of employing some type of transformation reaction as described in the literature and previously used in our lab[1], where an anionically synthesized polymer is used as the basis for a Ziegler-Natta catalyst (i.e. n-PolybutadieneLi/ $TiCl_4$) for stereospecific placement of the second block monomer. The basis of our isotactic polystyrene synthesis research was a body of prior research[3,4,5,6] conducted on the synthesis of polystyrene which showed that the addition of small quantities of water to the anionic polymerization of styrene conducted at very low temperatures resulted in partial conversion to isotactic polymer. This was attributed to an associative effect between the living polystyryl anion and the water molecules/lithium ion which, combined with the non-polar enviroment and slowed kinetics, acts as a kind of homogeneous stereospecific catalyst. Based on this association concept, we felt that the effect could be duplicated using associating agents other than water. As shown below, lithium- t-butoxide, BuOLi, is very effective in this respect. By adding varying ratios of BuOLi to BuLi initiator under specified conditions, isotactic polymerization of styrene has been achieved in reasonable yields.

The isotactic polystyrene/polybutadiene diblock was then prepared by following one of two synthesis routes: 1) sequential polymerization of the buta-diene followed by the styrene monomer, and 2) endcapping individual homopoly-mers with either a carboxylic acid or amine endgroup, followed by a condensation reaction to produce a well defined block copolymer structure.

EXPERIMENTAL

All reagent purification and subsequent synthesis were conducted using a vacuum/inert gas set-up. The vacuum was provided by a manifold equipped with Teflon/O-ring valves which, through a vacuum pump and oil diffusion pump could maintain better than 10^{-5} torr vacuum. The argon gas (>99.999% ultra high purity Matheson Gas) was passed through a 4X molecular sieves column followed by a

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deoxifying BASF copper based catalyst column before being utilized in flushing reactors and maintaining an inert gas blanket for the polymerizations.

The purification of styrene monomer involved removal of inhibitor by washing in a 10% NaOH solution, followed by distilled water wash and subsequent drying over calcium hydride. The monomer was then stored in the freezer in a flask containing Bu_2Mg, which reacts to produce living oligomers of a yellowish color which serve as an indication for monomer purity.

The butadiene monomer was likewise washed with a 10% NaOH solution, collected over calcium hydride at -78^oC, then vacuum distilled through a series of flasks containing fresh sodium mirrors before being placed in the freezer. This monomer was likewise stored with appropriate amounts of Bu_2Mg to insure purity.

The solvent, n-hexane, was dried over calcium hydride and subsequently fractionated, with the middle 80% recovered and stored under vacuum over a sodium dispersion.

The initiator for the anionic synthesis was n-BuLi, 2.5M in hexanes as aquired by Aldrich Chemicals, titrated with sec-butanol in xylene. The BuOLi was either aquired from Aldrich as a powder and dissolved in hexane prior to addition to the reactor, or directly prepared in specific ratios of BuOLi/BuLi as described in the literature[7].

SYNTHESIS

Sequential Synthesis

Due to the unknown details of the chemistry of the isotactic polystyrene/ BuOLi synthesis, and in order to facilitate separation of diblock from terminated first block homopolymer, the preferred approach to sequential diblock preparation for the iPS/PBD polymer was to synthesize the polybutadiene first, using this "living" material as the initiator for the styrene polymerization. The first reactor, consisting of a 500 ml flask with a gas entry port and a small septum port, was initially cleaned with hydrofluoric acid, rinsed with distilled water, dried, connected to the high vacuum line and pumped down while simultaneously being heated by a methane/oxygen flame in order to remove any SiOH groups and/or adsorbed water. The butadiene monomer and hexane solvent were vacuum distilled directly into the reactor. The polymerization solution was stirred by means of a small teflon stirbar in connection with a Lab-Line external magnetic stirrer. The temperature of the system was kept at $\approx 0^oC$ with ice water to reduce butadiene monomer pressure. Appropriate amounts of initiator were added by means of a gas tight syringe through the small septum port. The temperature was then raised to 50^oC and the reaction allowed to proceed for ≈ 24 hrs.

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A second reactor consisted of a 250 ml flask with a gas inlet valve, a septum port and a central shaft to accomodate an external stirrer. Styrene monomer and solvent.were introduced through vacuum distillation from respective storage flasks. The BuOLi solution (0.77 M) solution was added with a gas-tight syringe in an amount approximately equal to a 1:1 ratio with the living polybutadiene-lithium "initiator" which at this point was still stored in the first reactor. The temperature of reactor two was then lowered to ~ 0°C using an isopropanol bath equipped with a Neslab cryogenic cooler offset by a immersion heater. The living polybutadiene was then displaced into this flask with a cannula using argon overpressure, and the final polymerization temperature was set at ~ -30°C. The reaction was allowed to proceed for ~ 2-3 days, after which it was terminated by the addition of a few cc. of degassed methanol.

Condensation Reaction

The procedures for the synthesis of the individual homopolymers to be used for the coupling reaction are the same as stated in the previous section, with the polymerization of styrene initiated directly by BuLi in the presence of BuOLi. In each case, however, the reaction was not terminated with methanol but rather by an appropriate endfunctionalizing agent. For polybutadiene, bone dry carbon dioxide gas was bubbled into the reactor to provide a carboxylic acid end group for the polymer. Tetrahydrofuran was added prior to this to prevent coupling reactions[8]. Endfunctionalization was checked by titrating with a 0.01 M KOH solution[9].

For polystyrene, the chosen endfunctionalizer was N-(benzylidene)trimethyl-silylamine as prepared by the method of Kruger, Rochow and Wannagat[10]. Titrations were conducted using perchloric acid in glacial acidic acid with crystal violet indicator[11]. This reagent was added directly to the reaction in molar excess. The polymer was then recovered in methanol, dried, dissolved in xylene at elevated temperatures in order to force the isotactic polystyrene into solution (~100°C) and then hydrolyzed with dilute acid (pH 3-5 using HCL in a 75% hydrocarbon/25% water v/v solvent) in order to cleave the silyl group, thereby resulting in an amine terminated polymer[12]. This was was then refluxed in methyl ethyl ketone using a Sohxlet extractor, with the insoluble portion (~ 10% of original monomer content) recovered as the desired isotactic polymer.

The condensation reaction was conducted in dry xylene under inert argon atmosphere conditions to prevent polybutadiene oxidation. A molar excess of the easily separated polybutadiene was used to shift equilibrium towards diblock formation.

A summary of the polymerization conditions is given in Table I.

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TABLE I: Polymerization Conditions

Sample	Block	Solvent	Polym. Temp°C	Initiator	Endcapped with	Purification procedure
DSB6 (Coupled)	PBD$^\ominus$	Hexane	50 °C	n-BuLi	CO_2	Extracted PBD homopolymer with MEK
	iPS$^\ominus$	Hexane	-30 °C	n-BuLi/BuOLi	$C_5H_6CHNSi(CH_3)_3$	
DSB7 (Sequential)	PBD$^{\ominus *}$	Hexane	50 °C	n-BuLi	not terminated	MEK extraction of aPS/PBD block and PBD homopolymer
	iPS$^\ominus$	Hexane	-30 °C	PBD$^{\ominus *}$/BuOLi	MeOH	

$^\ominus$ living polymer

* living polybutadiene used in DSB7 block synthesis

Diblock and Homopolymer Purification and Characterization

For the condensation reaction, the two endfunctionalized homopolymers were accurately characterized prior to diblock formation. ^{1}H NMR spectra of the polybutadiene segments for the diblocks was consistent with the expected ~90% 1,4 and ~10% 1,2 microstructure typical of anionic synthesis of butadiene in a non-polar solvent. The molecular weight of the polybutadiene polymer was characterized by GPC for the case of both diblock preparation routes; an aliquot of living polybutadiene was removed and terminated prior to the addition of styrene monomer in the sequential polymerization.

The polystyrene block was characterized more extensively. ^{13}C NMR is useful in specifying the tacticity of the sample: in the range of 140-150 ppm, it is possible to differentiate three peaks for isotactic, atactic and syndiotactic polystyrene (146.8, 146.0, 145.5 ppm respectively)[6]. In the case of the condensation method, the endfunctionalized isotactic polystyrene homopolymer was isolated prior to diblock formation by removing the atactic material with refluxing MEK using a Sohxlet extractor for several days until the ^{13}C NMR spectra gave indication of essentially totally isotactic material (around 20% of the polymerization product). An example of the results is given in Fig.1. Molecular weight was determined by using either a 100A Waters GPC with 10^3, 10^4, and 10^5 molecular weight columns at room temperature with xylene as the solvent phase, or a Waters 150C GPC at ~100°C in toluene.

For the sequential diblock, all atactic product was extracted using several volumes of MEK at room temperature. The remaining material was analyzed with ^{13}C NMR and ^{1}H NMR was used to obtain the composition of the copolymer by observing the ratio of the peak integrations for the aromatic protons (~7.0 ppm) and for the saturated and unsaturated protons in the polybutadiene block; since the polybutadiene block was separately characterized by GPC, the number average molecular weight of the isotactic polystyrene could be derived from the information on the iPS/PBD ratio obtained from NMR. This ^{1}H NMR technique was also used in determining the effectiveness of the condensation reaction. After extracting the polybutadiene homopolymer with MEK, and having previously calculated the molecular weights for both blocks through GPC analysis, the weight ratio of iPS to PBD obtainable through ^{1}H NMR gives an indication of the diblock vs. iPS homopolymer content of the final material.

Thermal analyses were conducted on all polymers using a Perkin-Elmer DSC-IV instrument. Samples were prepared by placing a finely granulated powder of the copolymer as recovered from the purification process by precipitation into

methanol. Where possible, T_g and T_m were examined for both the individual homopolymers and then for the diblocks. Percent crystallinity was calculated assuming the following relationship:

$$\% \text{ crystallinity} = \Delta H_f / \Delta H_f^* * 100$$

where $\Delta H_f^* = 20.65$ cal/g is the heat of fusion for a perfectly crystalline iPS material[13]. Characterization results are sumarized in Table II.

Transmission electron microscopy provided visual verification of diblock structure. Thin samples were prepared by pressing some of the polymer between two microscope slides and applying varying thermal histories using a high temperature VWR 1410D vacuum oven. After staining the rubbery phase with 1% OsO_4 solution, ultramicrotomed sections were collected on 200 mesh copper specimen grids and examined with a Philips 300 TEM.

TABLE II: Polymer Characterization

Sample	Wt% iPS	Wt% PBD	Mn iPS	Mn PBD	$T_m^{iPS}(°C)$	$T_g^{iPS}(°C)$	$T_g^{Block}(°C)$	% crystallinity
DSB6 (Coupled)	81.7	18.3	45,000	11,000	216	97	- - -	15 - 20
DSB7 (Sequential)	81.6	18.4	20,000	4,500	208	92	60	8-10

RESULTS AND DISCUSSION

The two synthesis methods described here both lead to distinct, two block copolymers of isotactic polystyrene and polybutadiene. The sequential synthesis method starts off with a well characterized polybutadiene block upon which isotactic polystyrene chains are grown. For the condensation reaction case, the two-block nature is apparent as long as the coupling reaction proceeds. Separating the isotactic polystyrene/polybutadiene material from any homopolymers or atactic diblock which are byproducts of the copolymer synthesis is an important and needed step in both cases.

For DSB7 (sequential synthesis), GPC analysis gave an estimate of Mn = 4,500 g/mol for the polybutadiene chain. The degree of success of the extraction of atactic polystyrene (along with polybutadiene homopolymer) using MEK at room temperature was estimated using repetitive ^{13}C NMR analysis until a single peak was observed in the isotactic range of 146.8 ppm and the atactic peak at 146.0 ppm had essentially disappeared. Since styrene polymerization could only have been initiated by living polybutadiene chains, the resulting material may be reasonably assumed to be a diblock structure, but total elimination of the possibility of the product being a simple homopolymer blend requires the TEM evidence provided below. Using ^{1}H NMR, the polystyrene number average molecular weight was estimated to be = 20,000 g/mol.

For DSB6 (coupling synthesis), characterization of the homopolymers was conducted prior to condensation. The Mn of the polybutadiene chain was determined as = 11,000 g/mol, with % endfunctionalization essentially 100%. The isotactic polystyrene Mn was determined as = 45,000 g/mol, with again nearly 100% amine endfunctionalization. DSB6 was harder to purify due to the difficulty in separating iPS homopolymer (extracted prior to coupling) from the isotactic diblock, as washing with MEK would only extract the atactic polybutadiene homopolymer. However, by using the relative ^{1}H NMR proton peak intensities for polystyrene and polybutadiene, it was determined that the weight ratio of iPS/PBD in the final purified product closely approached that of the theoretically pure diblock sample (see Table II). Although as mentioned above this cannot be used as unequivocal proof of diblock formation, as it could in principle apply to a blend as well, when combined with other evidence (such as the following TEM results), it gives a very good indication the success of the coupling reaction.

Thermal analysis provides a better insight regarding the block-like nature of the two copolymers. DSB6 displays a glass transition temperature around 97°C, a melting point of 216°C with a crystallinity of approximately 15-20%. Granger

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and coworkers have measured a depressed T_g of around 90°C for the phase separated polystyrene content of PS/PBD block copolymers compared to the PS homopolymer[14]. Since our DSB6 T_g is only a few degrees lower than the 100°C observed for the iPS4 homopolymer prior to condensation, this leads us to believe that the purification process was incomplete for DSB6 and that a certain homopolymer content is present in our sample. TEM photographs support this assumption as will be shown later.

Thermal analysis of DSB7 provided a T_g of approximately 92°C, a melting point of 208°C with a crystallinity of 8-10%. Even though the glass transition temperature will decrease slightly for a lower molecular weight polystyrene block, this depressed T_g is taken as a good indication of higher diblock content as compared to DSB6. Furthermore, a transition is also observed around 60°C. This corresponds roughly to the weighted average of the two homopolymer glass transition temperature, implying that the copolymer precipitated in part as a homogeneous sample. Upon reaching the copolymer T_g, however, the sample reverts to a thermodynamically favored microphase separated morphology. After bringing the sample above T_m and subsequently quenching in liquid nitrogen, the 60°C transition disappeared, while the 92°C T_g was strongly reinforced. This implies that the transition from the ordered phase separated morphology to the disordered homogeneous state is achieved above the glass transition and is too fast to be effectively quenched. While several researchers have been able to identify this transition by means of SAXS and dynamic mechanical measurements, the effect appears to be too small to be analyzed by DSC[15]. As for our case of DSB7, it was also noted that the the shift from ordered microstructure to disordered phase is very rapid and it was not possible to heat a sample above the transition point and quickly quench it in liquid nitrogen to freeze the homogeneity for subsequent TEM visual identification[16]. It will therefore be necessary for us to resort to other analysis such as SAXS or possibly the Rheovibron for dynamic mechanical analysis to observe this effect.

Theoretical investigations regarding the thermodynamics of phase separation in block copolymers have been carried out by a number of researchers in recent years (i.e Meier, Helfand, Roe, Noolandi, Liebler). A very useful program for determining domain sizes in block copolymer systems has been provided by Helfand and Wasserman[17], based on their Narrow Interface Approximation (NIA). For the often quoted 7-43-7 PS/PBD triblock copolymer, the resulting T_{trans} of 141°C as given by a modified version of the Helfand program is in good agreement with the transition in the viscoelastic properties of that block copolymer at approximately 138-146°C observed by Gouinlock and Porter[15]. As a first approximation, then, this modified program was used to predict the transition temperature for our

particular blocks. For the case of DSB6, T_{trans} is calculated to be around 75°C. This falls just above the expected T_g as observed for the homogeneous sample, and as shown by DSC results and subsequent TEM pictures, this phase transition is too rapid for the homogeneity to be frozen in the system by liquid nitrogen quenching. For DSB6, T_{trans} is approximately 250°C and in this case occurs slightly above the melting point of the crystalline regions. Competion between the kinetics of crystallization and the thermodynamically driven phase separation could become important in this area. Further studies need to be conducted by preparing samples whose transition temperatures are more easily identifiable and do not interfere with the crystallization process.

Transmission electron microscopy provides visual proof regarding the diblock nature of our polymers. At lower temperatures, it has been demonstrated that diblock copolymers exhibit heterogeneous domain morphology. Depending on the molecular weight of the respective blocks, spherical, cylindrical or lamellar regions of one material in a matrix of the other can be observed. For the case of our two diblock copolymers, the expected morphology is that of polybutadiene spheres in a polystyrene matrix. These spheres are expected to fall in the ~50-150 Å size range, with larger domains indicating either larger scale phase separation of homopolymers or possibly an emulsification effect of the diblocks on the incompatible blend.

Fig.2 is a TEM photograph of a DSB6 sample prepared by bringing the sample to approximately 240°C for 1/2 hr. and subsequently quenching in liquid nitrogen (darker regions are stained polybutadiene). What is immediately obvious is the lack of a very finely distributed and very ordered microstructure. Rather, the photograph substantiates the original observations made by DSC that the condensation reaction was not totally successful and that there is still a certain amount of homopolymer, both iPS and PBD, present in the final sample. Though small spheres in the correct size range are observed, there are larger pools of polybutadiene indicating gross phase separation. Other areas of the same sample, however, show a definite microphase separated system with spheres in the 50-100Å range Fig.3). This non-uniformity in our sample is attributed to the preparation technique: for future studies, static cast films of the copolymers will be prepared from toluene solutions in order to eliminate this problem. Nonetheless, the TEM results are encouraging in that they point toward the presence of diblock copolymer in our system. Options are presently being considered in how to improve the effectiveness of the condensation reaction in preparing the next samples.

Due to the synthesis method used, DSB7 is expected to display a much more pronounce diblock structure. As shown in Fig.4 the sample consists primarily of a

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fine dispersion of polybutadiene spheres in the polystyrene matrix. This is reflected throughout the whole sample and is not an isolated observation. Though it can be assumed that there is a certain small concentration of polybutadiene homopolymer chains terminated prior to styrene addition, these are assumed to have been incorporated into the polybutadiene domains.

FUTURE WORK

Further work is now being conducted in synthesizing more diblocks by the two methods described in this report. The condensation synthesis procedure will be modified by the addition of 1-hydroxybenzotriazole according to the directions of Gnanou and Rempp[18], as this should shift the equilibrium to higher degrees of diblock conversion. More care is also being used in the preparation of static cast films for ultramicrotoming work in order to provide better samples with more distinct and representative phase separation than the precipitated/pressed polymer samples used up to now. Larger conversions of isotactic polymer (homopolymer and diblock) will permit studies on crystallization behavior and blend morphology. Thin strip samples will be prepared and information regarding dynamic visco- elastic responses can be obtained using the Rheovibron. By preparing a special vacuum holder with temperature control, SAXS is also a possibility for studying the heterogeneous-homogeneous transition and crystallization effects in our diblock copolymers.

References

1   M.A. Drzewinski and R.E. Cohen, **J. Polymer Sci., Chemistry**, 24, 2457 (1986).

2   L. DelGiudice, R.E. Cohen, G. Attala and F. Bernotti, **J. Appl. Poly. Sci.**, 30, 4305 (1985).

3   R.J. Kern, **Nature**, 187,410 (1960).

4   K. Gehrke and C. Roth, **Plaste und Kautschuk**, 7, 493 (1973).

5   D.J. Worsfold and S. Bywater, **Makromol. Chem.**, 65, 245 (1963).

6   T. Kawamura, T. Uryu and K. Matsuzaki, **Makromol. Chem.**, 180, 2001 (1979).

7   J.E. Roovers and S. Bywater, **Trans. Faraday Soc.**, 62, 1876 (1966).

8   Roderic P. Quirk and Wei-Chih Chen, **Makromol. Chem.**, 183, 2071 (1982).

9   L.C. Anand, A. Takahashi, N.G. Gaylord, **Macromol. Synth.**, 4, 9 (1972).

10 C. Krüger, E.G. Rochow, U. Wannagat, **Chem. Ber.**, 96, 1962 (1963).

11 M. Sela, A. Berger, **J. Am. Chem. Soc.**, 77, 1893 (1955).

12 D.N. Schulz and A.F. Halasa, **J. Polym. Chem., Polym. Chem. Ed.**, 15, 2401 (1977).

13 **Polymer Handbook,** J. Brandup, E.H. Immergut, eds., John Wiley & Sons, New York, 1975.

14 A.T. Granger, B.Wang, S. Krause and L.J. Fetters, in **Multicomponent Polymer Systems,** Advances in Chemistry Series 211, D.R. Paul and L.H. Sperling, eds., American Chemical Society, Wash. D.C. 1986.

15 E.V. Gouinlock and R.S. Porter, **Polym. Eng. Sci.**, 17, 535 (1977).

16 Ryong-Joon Roe, M. Fishkis and J.C. Chang, **Macromolecules**, 14, 1091 (1981).

17 E. Helfand and Z.R. Wassaerman, in **Developments in Block Copolymers - I**, I. Goodman, ed., Applied Science Publ., 1982.

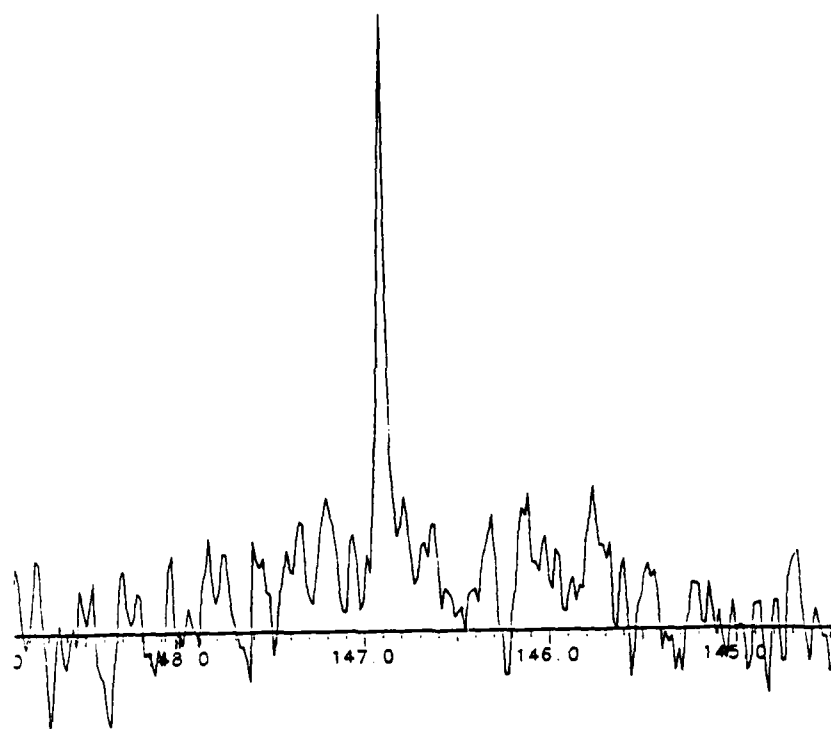18 Y. Gnanou and P. Rempp, **Makromol. Chem.**, 188, 2111 (1987).

Figure 1. ^{13}C NMR of isotactic polystyrene
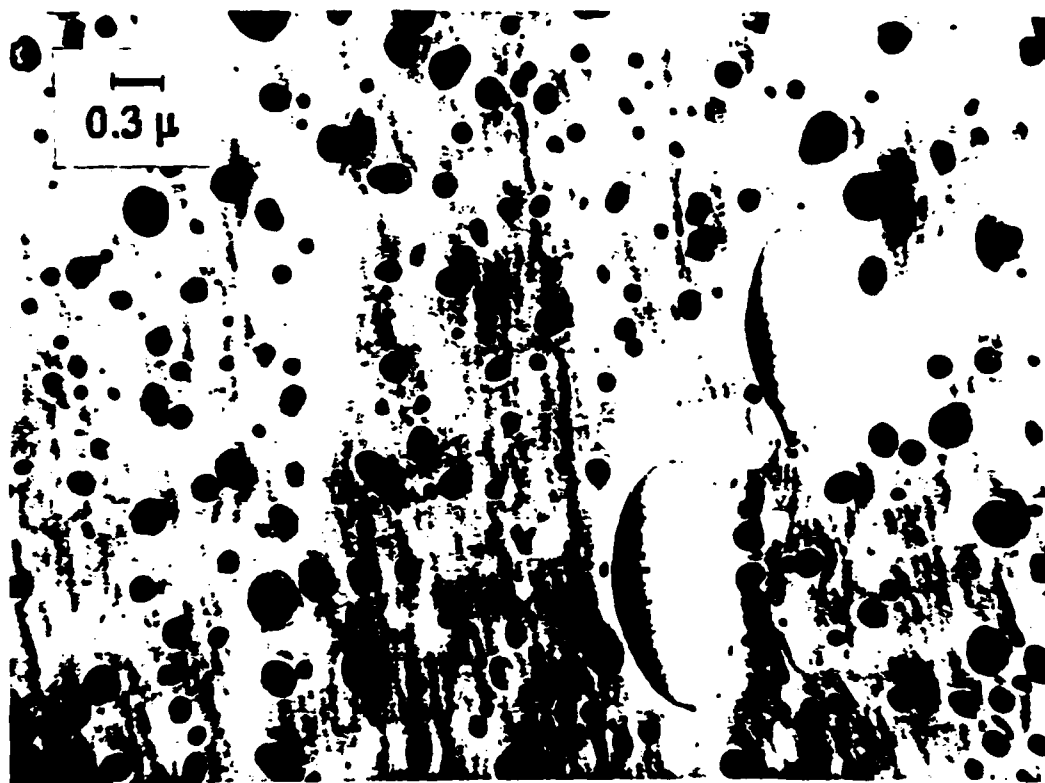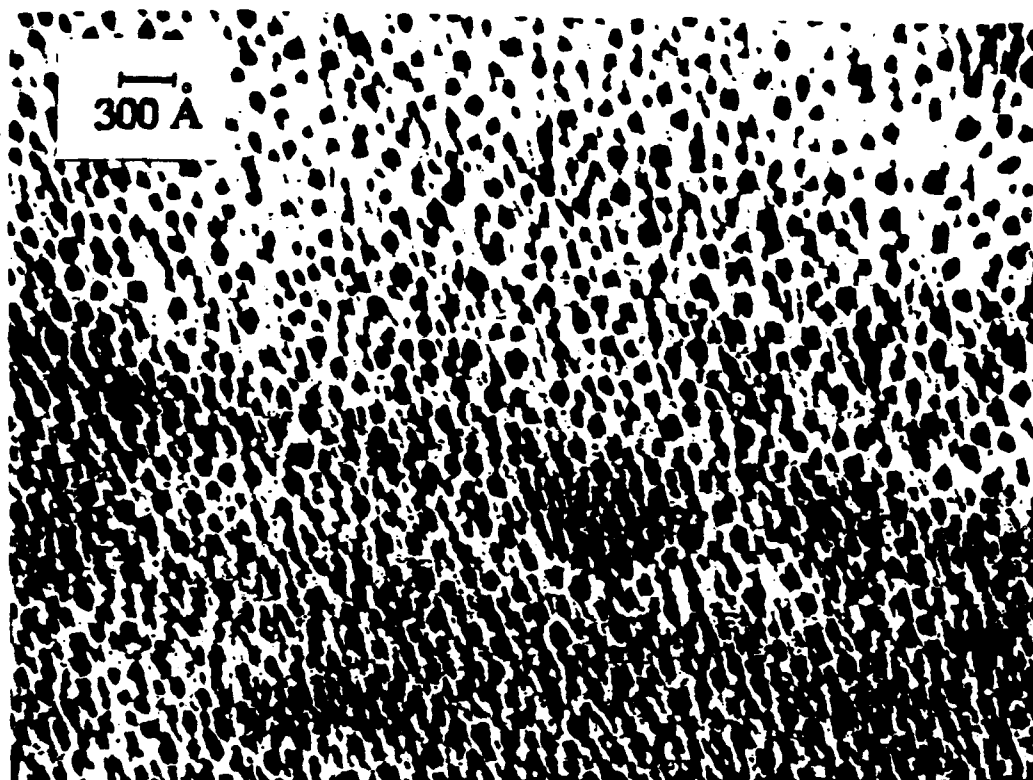

Fig. 2 Transmission electron micrograph of DSB6

Fig. 3   Transmission electron micrograph of DSB6

Fig. 4   Transmission electron micrograph of DSB7

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